

# Photodetachment of $F^-(H_2O)_n$ ( $n=1-4$ ): Observation of charge-transfer states $[F^-(H_2O)_n]^+$ and the transition state of $F+H_2O$ hydrogen abstraction reaction

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We report a photoelectron spectroscopic study of  $F^-(H_2O)_n$  ( $n=1-4$ ) at 193 and 157 nm. In addition to a detachment feature from  $F^-$ , we observed a higher binding energy feature in all spectra due to ionization of the solvent molecules leading to  $F^-(H_2O)_n^+$  charge-transfer states. Detachment of an electron from  $F^-$  in  $F^-(H_2O)$  reaches the transition state region of the reaction,  $F+H_2O \rightarrow HF+OH$ . The bound to non-bound transition resulted in a long tail at the low binding energy side in the photoelectron spectrum of  $F^-(H_2O)$ . We estimated that the neutral  $F \cdots H_2O$  complex at the anion geometry, which is near the transition state region of the H-abstraction reaction, is  $6 \pm 1$  kcal/mol above the  $F+H_2O$  asymptote, consistent with a previous estimation of a 4 kcal/mol entrance barrier height for this reaction. © 2001 American Institute of Physics. [DOI: 10.1063/1.1394758]

The study of solvated ionic clusters provides molecular level information about interactions between the solvent and solute molecules. The structures and energetics of small ion-water clusters are of particular interest because they provide benchmarks in the development and parameterization of interaction potentials for modeling ionic solvation processes. The solvation of simple halide anions has been a favorite subject for an increasing amount of experimental and theoretical studies lately.<sup>1-7</sup> The  $F^-$  anion is special and different from all the other halide anions. The interaction of  $F^-$  with  $H_2O$  is so strong that  $F^-$  tends to be solvated in the center of the water clusters,<sup>2,6,7</sup> whereas all the other halide anions prefer to locate on the surface of the water clusters.<sup>4,5</sup> The ground state structures of  $F^-(H_2O)_n$  have been investigated by infrared spectroscopy near the O-H stretching frequencies,<sup>1,2</sup> as well as high-level *ab initio* calculations.<sup>2,5-7</sup> The fluoride ion-water bond energy<sup>8</sup> has been determined more accurately very recently.<sup>9</sup>

Photoelectron spectroscopy (PES) is a valuable technique to probe solvated anion clusters and can provide important energetic information. Indeed, Cheshnovsky *et al.*<sup>10</sup> have reported a PES study of  $X^-(H_2O)_n$  ( $X=Cl, Br, \text{ and } I$ ), not including  $F^-(H_2O)_n$ , presumably due to their small detachment cross sections and/or extremely high electron binding energies. The  $F^-(H_2O)_n$  systems, however, are of particular interest. There has been a theoretical prediction of a charge-transfer (CT) state ( $F^-H_2O^+$ ) at a vertical binding energy (VDE) of 5.75 eV from  $F^-(H_2O)$ .<sup>11</sup> Analogous CT states were observed in PES spectra of  $Cl^-(NH_3)$  and other amine ligands.<sup>12,13</sup> Despite the theoretical prediction of the rather low VDE for the CT transition from  $F^-(H_2O)$ , it has

not been observed experimentally. Furthermore, the  $F+H_2O \rightarrow HF+HO$  reaction, is exothermic ( $\Delta H_{298}^\circ = -17.2$  kcal/mol), contrary to the endothermic hydrogen abstraction reactions of the other halogen atoms (Cl, Br, I) with  $H_2O$ .<sup>14</sup> A previous kinetic and mechanistic investigation of  $F+H_2O$  obtained a 4 kcal/mol entrance barrier,<sup>15</sup> which may be accessed by photodetachment of  $F^-(H_2O)$ . Similar hydrogen abstraction reactions of  $F + \text{alcohol}$  ( $CH_3OH$  and  $C_2H_5OH$ ) were studied previously using photodetachment transition state spectroscopy by Neumark *et al.*<sup>16</sup> Here we report the first PES study of  $F^-(H_2O)_n$  ( $n=1-4$ ) and the observation of the charge-transfer states in the solvated clusters. The nearly linear F-H-O bond in  $F^-(H_2O)$  due to the strong H-bonding interaction allowed photodetachment to reach the vicinity of the transition state region of the  $F+H_2O \rightarrow HF+HO$  reaction. From the measured VDE of  $F^-H_2O$ , we were able to estimate the entrance barrier for the hydrogen abstraction reaction.

The  $F^-(H_2O)_n$  anion clusters were produced by an electrospray source and details of the experimental setup have been published elsewhere.<sup>17</sup> Briefly, a  $10^{-4}$  M sodium fluoride salt solution in a  $H_2O/CH_3CN$  (20/80 ratio) mixed solvent was sprayed at ambient conditions through a 0.01 mm diameter needle biased at  $-2.2$  kV. The resulting negatively charged droplets were fed into a 3 cm long, 0.5 mm inner diameter desolvation capillary heated to  $\sim 50^\circ C$ . Anionic species emerged from the desolvation capillary were guided by a radio-frequency quadrupole system into a quadrupole ion trap. The anions were accumulated in the ion trap for 0.1 s before being pushed into the extraction zone of a time-of-flight (TOF) mass spectrometer. The  $F^-(H_2O)_n$  clusters of interest were selected and intercepted by a 193 (6.424 eV) or 157 nm (7.866 eV) laser beam in the detachment zone of a magnetic-bottle TOF photoelectron analyzer. The experiment

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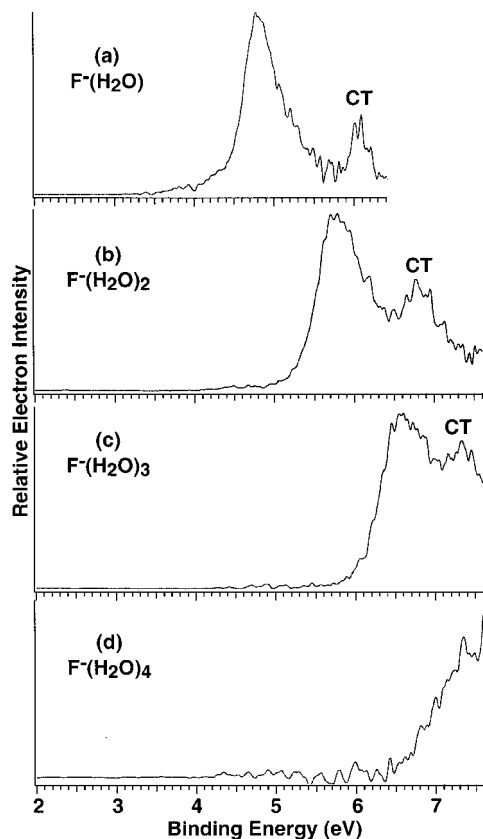


FIG. 1. Photoelectron spectra of  $F^-(H_2O)_n$  at 193 nm (6.424 eV) for  $F^-(H_2O)$  (a) and 157 nm (7.866 eV) for (b)  $F^-(H_2O)_2$ , (c)  $F^-(H_2O)_3$ , and (d)  $F^-(H_2O)_4$ . CT represents charge-transfer transitions (see text).

was done at 20 Hz repetition rate with the ion beam off at alternating laser shots for background subtraction. The photoelectron TOF spectra were converted to kinetic energy spectra calibrated by the known spectra of  $I^-$  and  $O^-$ . The energy resolution of the apparatus was about 11 meV at 0.4 eV kinetic energy, but deteriorated significantly at 193 and 157 nm both due to the laser bandwidth and the strong background present at these wavelengths.

Figure 1 shows the PES spectra of  $F^-(H_2O)_n$  ( $n = 1-4$ ). The  $F^-(H_2O)$  ion intensity was very weak due to the transmission of our quadrupole ion-guide at lower masses and its spectrum was only taken at 193 nm, where the photon flux was high. The electron affinity of F atom is 3.401 eV<sup>18</sup> and F has a very small spin-orbit splitting (51 meV).<sup>19</sup> Thus we expected to observe only one broad PES band due to the unresolved spin-orbit splitting of F. Surprisingly, we observed two well-separated bands in all the spectra and the intensity of the second band increased with  $n$ . The VDEs of  $F^-(H_2O)_n$  increase very rapidly with  $n$ , and the second band of  $F^-(H_2O)_4$  already exceeded the photon energy at 157 nm. All the spectra appeared to show a long tail at the low binding energy side, particularly for  $F^-(H_2O)$ . The VDEs of each observed band, measured from the peak maximum, are given in Table I.

The  $F^-$  ion should maintain its atomic characteristics in the solvated clusters and only one detachment band due to the unresolved spin-orbit states of F was expected for the PES spectra of the  $F^-(H_2O)_n$  clusters, as were the cases for

TABLE I. Observed vertical (VDE) detachment energies for the  $F^-$  channel and the charge-transfer (CT) states from the photoelectron spectra of  $F^-(H_2O)_n$  ( $n = 1-4$ ). Energies are all in eV.<sup>a</sup>

$n$	VDE	VDE (CT)
1	4.80 (5)	6.10(10)
2	5.79(10)	6.80(10)
3	6.59(10)	7.32(10)
4	7.35(20)	>7.6

<sup>a</sup>The VDEs were measured from the peak maximum of each photodetachment feature. The numbers in the parentheses indicate the uncertainties in the last digits.

the heavier halides (Fig. 2). The second band in the spectra of  $F^-(H_2O)_n$  was attributed to the anticipated CT state, predicted to occur at a VDE of 5.75 eV for  $F^-(H_2O)$ .<sup>11</sup> The predicted VDE for the CT transition of  $F^-(H_2O)$  is apparently too low by  $\sim 0.35$  eV, compared to our measured value of 6.10 eV. A CT transition was also predicted for  $Cl^-(H_2O)$  at a VDE of 7.19 eV,<sup>11</sup> which is also too low, because our PES spectrum of  $Cl^-H_2O$  [Fig. 2(b)] did not show the anticipated CT band even at 157 nm (7.866 eV). Two changes were observed for the CT band in the large  $F^-(H_2O)_n$  clusters: Its intensity increased and its separation from the PES band due to  $F^-$  decreased. The CT band is due to the ionization of the solvent, producing  $F^-(H_2O)_n^+$  ion pairs. Thus the two observed changes of the CT band in the large solvated clusters are understandable because each solvent molecule is expected to contribute to the CT band.

The observation of the CT transitions in the  $F^-(H_2O)_n$  systems is both interesting and remarkable, considering the very high ionization potential (IP) of free  $H_2O$  molecules (12.6 eV).<sup>20</sup> The previous theoretical predictions for the

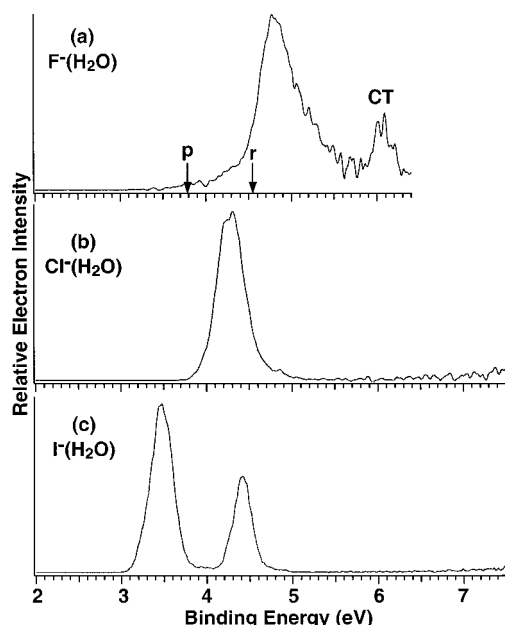


FIG. 2. Photoelectron spectra of  $F^-(H_2O)$  at 193 nm (a), compared to the spectra of  $Cl^-(H_2O)$  (b) and  $I^-(H_2O)$  (c) at 157 nm. The arrows,  $p$  and  $r$ , indicate energies corresponding to product ( $HF+OH$ ) and reactant ( $F+H_2O$ ) asymptotes (see Fig. 3).

VDEs of CT transitions were based on *ab initio* calculations. Since the occurrence of the CT transition is largely an electrostatic effect, it can also be understood based on simple electrostatic considerations. The VDE of the CT band is due to the ionization of  $H_2O$ , whose IP is reduced in the solvated complexes due to the strong Coulomb repulsion from the negative charge of  $F^-$ . The IP reduction of  $H_2O$  in  $F^-(H_2O)$  can be approximately estimated by considering the Coulomb repulsion between  $F^-$  and an electron from the highest occupied molecular orbital (HOMO) of  $H_2O$ ,  $e^2/r$ , where  $r$  is the distance between  $F^-$  and O in  $F^-(H_2O)$ . Taking  $r=2.452$  Å,<sup>11</sup> we evaluated the VDE of the CT band to be 6.7 eV [ $IP(H_2O)-e^2/r$ ], only about 0.6 eV higher than the measured value, indicating the importance of the electrostatic effect. In fact, the electrostatic effect observed here for the solvated species is analogous to our previous observation of intramolecular Coulomb repulsions in multiply charged anions with localized charges. For example we observed that the negative electron binding energy observed in copper phthalocyanine tetrasulfonate tetraanion  $[CuPc(SO_3)_4]^{4-}$  was due to the strong Coulomb repulsion felt by the HOMO electrons of the CuPc neutral parent molecule from the four peripheral negative charges ( $-SO_3^-$ ).<sup>21</sup> A simple electrostatic model also yielded reasonable agreement with experimental observations.<sup>21</sup>

As reported previously by the Neumark and Lineberger groups,<sup>16,22-25</sup> PES of anions is a valuable technique to probe transition state properties of chemical reactions, if appropriate anion precursors can be prepared. The final states of photodetachment are neutrals, which may be near the transition state region of a chemical reaction. The global minimum structure of the  $F^-H_2O$  complex has  $C_s$  symmetry with a strong and nearly linear F-H-O bond.<sup>8</sup> Figure 3 shows that the  $[FH_2O]$  neutral complex accessed from detachment of  $F^-(H_2O)$  is  $\sim 0.26$  eV above the  $F+H_2O$  asymptote. The transition state (TS) geometry of the  $F+H_2O$  H-abstraction reaction was calculated to have  $C_1$  symmetry with a  $124^\circ \angle F-H-O$  angle and a 1.29 Å  $F\cdots H$  bond distance (Fig. 3).<sup>15</sup> Therefore, the potential region of the  $[FH_2O]$  complex reached via vertical photodetachment of  $F^-(H_2O)$  is located about 0.1 Å away (toward the reactants) from the TS along the reaction coordinate on the  $F+H_2O$  potential energy surface. Nevertheless, the 0.26 eV (6.0 kcal/mol) barrier height estimated from the VDE of  $F^-(H_2O)$  agrees well with a predicted 4 kcal/mol classical barrier for this reaction,<sup>15</sup> suggesting that photodetachment of  $F^-H_2O$  indeed accessed the vicinity of the TS of the  $F+H_2O$  H-abstraction reaction.

As shown in Fig. 2, the spectrum of  $F^-(H_2O)$  was much broader with a long low binding energy tail relative to the spectra of  $Cl^-(H_2O)$  and  $I^-(H_2O)$ , even though the spectra were taken under identical source conditions. The width of the  $F^-(H_2O)$  spectrum is consistent with the fact that detachment reached the vicinity of the TS of the  $F+H_2O$  reaction. The two arrows, *r* and *p*, in Fig. 2(a) indicate the thermodynamic limits for the reactant ( $F+H_2O$ ) and product ( $HF+OH$ ) asymptotes, respectively. The long tail in the PES spectrum of  $F^-H_2O$  was most likely due to coupling to the product channel (Fig. 3). Our observation for  $F^-H_2O$  is similar to that of previous PES studies of  $OHF^-$  and  $CH_3OHF^-$ ,

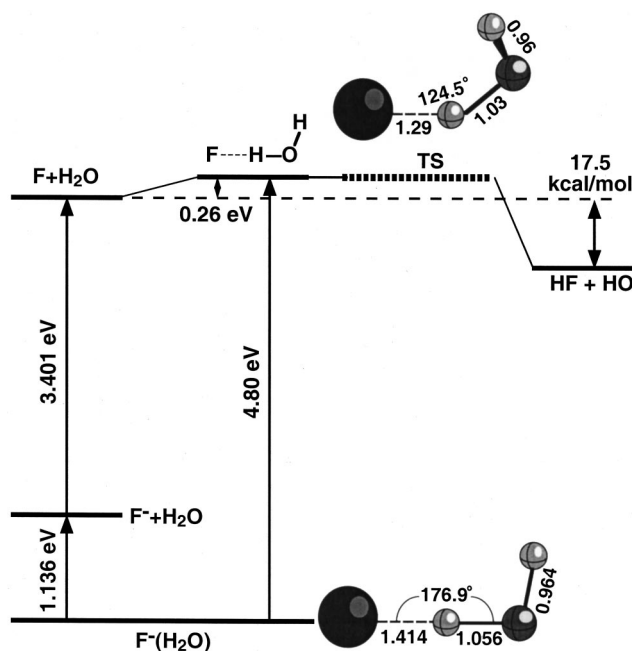


FIG. 3. A schematic diagram illustrating the thermodynamic relationship between the vertical detachment of  $F^-H_2O$  and the transition states (TS) of the  $F+H_2O$  H-abstraction reaction. The dissociation energy of  $F^-(H_2O)$  is from Ref. 9. The ground state structure of  $F^-(H_2O)$  is from Ref. 7 and the transition state geometry is from Ref. 15.

which also displayed long low binding energy tails corresponding to coupling to the  $O+HF$  or  $CH_3O+HF$  products after photodetachment.<sup>16</sup> Similar H-abstraction reactions for  $Cl+H_2O$  and  $I+H_2O$  are endothermic and no such coupling to product channels can occur in the photodetachment of  $Cl^-(H_2O)$  and  $I^-(H_2O)$ , consistent with the fact that no low binding energy tails were observed in their PES spectra (Fig. 2).

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<sup>1</sup>P. Ayotte, J. A. Kelly, S. B. Nielsen, and M. A. Johnson, *Chem. Phys. Lett.* **316**, 455 (2000); P. Ayotte, S. B. Nielsen, G. H. Weddle, and M. A. Johnson, *J. Phys. Chem.* **103**, 10665 (1999).

<sup>2</sup>O. M. Cabarcos, C. J. Weinheimer, J. M. Lisy, and S. S. Xantheas, *J. Chem. Phys.* **110**, 5 (1999).

<sup>3</sup>J. H. Choi, K. T. Kuwata, Y. B. Cao, and M. Okumura, *J. Phys. Chem. A* **102**, 503 (1998).

<sup>4</sup>D. J. Tobias, P. Jungwirth, and M. Parrinello, *J. Chem. Phys.* **114**, 7036 (2001).

<sup>5</sup>I. A. Topol, G. J. Tawa, S. K. Burt, and A. A. Rashin, *J. Chem. Phys.* **111**, 10998 (1999); L. S. Sremaniak, L. Perera, and M. L. Berkowitz, *J. Phys. Chem.* **100**, 1350 (1996).

<sup>6</sup>J. Kim, H. M. Lee, S. B. Suh, D. Majumdar, and K. S. Kim, *J. Chem. Phys.* **113**, 5259 (2000); J. Baik, J. Kim, D. Majumdar, and K. S. Kim, *ibid.* **110**, 9116 (1999); S. J. Vaughn, E. V. Akhmatkaya, M. A. Vincent, A. J. Masters, and I. H. Hillier, *ibid.* **110**, 4338 (1999).

<sup>7</sup>S. S. Xantheas and L. X. Dang, *J. Phys. Chem.* **100**, 3989 (1996); S. S.

- Xantheas and T. H. Dunning, Jr., *ibid.* **98**, 13489 (1994); S. S. Xantheas, J. Chem. Phys. **104**, 8821 (1996).
- <sup>8</sup>M. Arshadi, R. Yamdagni, and P. Kebarle, J. Phys. Chem. **74**, 1475 (1970).
- <sup>9</sup>P. Weis, P. R. Kemper, M. T. Bowers, and S. S. Xantheas, J. Am. Chem. Soc. **121**, 3531 (1999).
- <sup>10</sup>G. Markovich, P. Pollack, R. Giniger, and O. Cheshnovsky, J. Chem. Phys. **101**, 9344 (1994).
- <sup>11</sup>U. Kaldor, Z. Phys. D: At., Mol. Clusters **31**, 279 (1994).
- <sup>12</sup>G. Markovich, O. Cheshnovsky, and U. Kaldor, J. Chem. Phys. **99**, 6201 (1993).
- <sup>13</sup>G. Markovich and O. Cheshnovsky, J. Phys. Chem. **98**, 3550 (1994).
- <sup>14</sup>*CRC Handbook of Chemistry and Physics*, 76th ed., edited by D. R. Lide (CRC, Boca Raton, 1995), pp. 4–5.
- <sup>15</sup>P. S. Stevens, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **93**, 4068 (1989).
- <sup>16</sup>S. E. Bradforth, D. W. Arnold, R. B. Metz, A. Weaver, and D. M. Neumark, J. Phys. Chem. **95**, 8066 (1991).
- <sup>17</sup>L. S. Wang, C. F. Ding, X. B. Wang, and S. E. Barlow, Rev. Sci. Instrum. **70**, 1957 (1999).
- <sup>18</sup>H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **14**, 731 (1985).
- <sup>19</sup>S. Baskin and J. O. Stoner, Jr., *Atomic Energy Level and Grotrian Diagrams* (North-Holland, New York, 1978), Vol. 2.
- <sup>20</sup>S. G. Lias, in *CRC Handbook of Chemistry and Physics*, 76th ed., edited by D. R. Lide (CRC, Boca Raton, 1995), pp. 10–210.
- <sup>21</sup>X. B. Wang and L. S. Wang, Nature (London) **400**, 245 (1999); X. B. Wang, K. Ferris, and L. S. Wang, J. Phys. Chem. A **104**, 25 (2000).
- <sup>22</sup>D. M. Neumark, Acc. Chem. Res. **26**, 33 (1993).
- <sup>23</sup>D. E. Manolopoulos, K. Stark, H.-J. Werner, D. W. Arnold, S. E. Bradforth, and D. M. Neumark, Science **262**, 1852 (1993).
- <sup>24</sup>E. D. Beer, E. H. Kim, D. M. Neumark, R. F. Gunion, and W. C. Lineberger, J. Phys. Chem. **99**, 13627 (1995).
- <sup>25</sup>P. G. Wenthold, D. A. Hrovat, W. T. Borden, and W. C. Lineberger, Science **272**, 1456 (1996).